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SCANNING TUNNELING MICROSCOPY OF SEMICONDUCTOR SURFACES

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SCANNING TUNNELING MICROSCOPY OF SEMICONDUCTOR SURFACES

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ABSTRACT

In this final report, we discuss our recent results with the structure of metals on semiconductor surfaces. In particular, we focus our study on the use of surfactants for the epitaxial growth of germanium on silicon. A surfactant, such as tellurium, reduces the interfacial energy between the Si and Ge, as well as their surface free energies to change the growth mode to layer by layer, which is necessary to epitaxial growth. In addition to this summary of technical progress, we summarize some of the important events that took place in the Ginzton Lab during the period covered by this grant. These include the introduction of the force microscope and the transfer of this technology to industrial firms in such a way that instruments based on the designs developed under this grant are now available in commercial form. Finally, we point out that our work on microfabrication of silicon cantilevers can be extended to the construction of parallel arrays where each cantilever is operated independently. Such an array will enable a large increase in speed for the new form of lithography based on patterning silicon with the E-field on the scanning tip. Such patterning can produce lines with widths less than 0.1 μm . This range, beyond the limits of optical lithography, is of crucial importance to the future of silicon microcircuits.

INTRODUCTION

The main focus of this work has been to study surfactants for epitaxial growth of germanium on silicon. The 4.2% lattice mismatch between germanium and silicon results in the Stranski-Krastanov growth mode where the initial growth is layer by layer and additional Ge forms three-dimensional islands. A surfactant such as arsenic,[1] antimony,[2] or tellurium[3] reduces the interfacial energy between the Si and Ge, as well as their surface free energies, to change the growth mode to layer by layer, which is necessary for epitaxial growth. With an intermediate submonolayer to monolayer of a surfactant material, thick layers of Ge may be grown layer by layer on Si. The mechanism for the surfactant action is unknown. X-ray photoelectron spectroscopy (XPS) results show that the surfactant floats on top of the growing Ge layer during deposition.[4] Figure 1 schematically depicts the surfactant-mediated growth model.

We have used scanning tunneling microscopy (STM) to investigate surfactants on silicon, concentrating on low coverages of Te on both Si(111) and Si(100) surfaces. Higuchi and Nakanishi have shown, using RHEED, LEED, TEM, and SIMS, that Te on Si(111) acts as a surfactant for Ge epitaxial growth and does not remain at the Si/Ge interface.[3] Photoemission work

studying Te on Si(100) and growth of Ge on this system showed that only ~1/4 monolayer of Te is necessary for epitaxial growth of Ge on Si(100).[4] By using STM, which can image individual atomic positions on surfaces in real space, we hope to shed light on the mechanisms underlying surfactant-mediated epitaxial growth.

The Te/Si(100) System

An empty state STM image of 0.1 ML Te on Si(100) deposited at room temperature (RT) (Fig. 2) shows separated bright spots (indicating the tip was pulled away from the surface to maintain constant current) on top of the Si dimers which have a slight preference to form along the dimer rows. These spots appear in both unfilled (negative tip bias) and filled state (positive tip bias) images. Annealing this surface to approximately 400°C for ten minutes results in Te dimer zigzag chains running perpendicular to the underlying Si dimers, as shown in the positive bias image in Fig. 3. These zigzag chains have maxima (Te dimers) separated by one silicon lattice spacing a (a = 3.84 Å) located in the troughs of the underlying Si dimer rows. The minimum spacing of parallel zigzag chains observed is 2a . Si dimer rows in the region of the Te are disrupted by the Te; the Si dimers near the tellurium are usually buckled, indicating that Te stabilizes the silicon surface.[5] Dark lines perpendicular to the Si dimer rows extending from the Te chains often appear in the STM images. Similar "trenches" were seen in Sn/Si(100) samples and were hypothesized to be due to missing silicon in the Si dimers with the substitution of tin for Si along the trench edges forming Sn-Te dimers.[6] Likewise, it is believed that these trenches are due to the formation of Te-Si dimers. This is in agreement with Si core-level XPS spectra taken on similarly prepared samples, which for unannealed samples, have a single surface peak due to Si-Si dimers, and upon annealing, have a second surface peak shifted to higher binding energy due to the formation of Te-Si dimers.[4]

The Te/Si(111) System

An empty state STM image of 0.15 ML Te deposited at room temperature on Si(111) (Fig. 4) shows a preference for Te adsorption at adatom sites near the corner holes of the 7 x 7 unit cell at low coverage. In filled state images, the Te seems to enhance the contrast between the faulted and unfaulted halves of the unit cell. The unannealed and annealed surface look similar. This is in agreement with Si_{2p} core-level photoemission spectra (Fig. 5) that show that the Si_{2p} surface state peak increases slightly in relation to the bulk peak upon Te deposition, and that the spectra remain the same after annealing. Valence-band XPS spectra (Fig. 6) show that the intensity of the peak associated with the Si adatom site decreases with Te deposition, indicating that the Te is residing at the adatom site.[7]

Other Systems

Hydrogen and boron have also been shown to act as surfactants for Ge growth at low temperature.[8,9] We have directed some effort at studies of these systems with the STM, but with limited success. Both wet chemical treatments and in-situ gaseous treatments known to H-terminate the Si surface were tried, but acceptable atomic resolution images were not obtained. Decaborane was used as a boron source. After a mild anneal (500°C, 10 min), the decaborane decomposes with the hydrogen coming off the sample leaving behind the boron. Unfortunately, the decaborane can react at low voltage with nitrogen to form boron nitride.[9] This seemed to occur on the tip, causing the tip to become unrecoverably insulating. Photoemission work has shown that boron oxide (B_2O_3) is a good boron source where the oxygen is easily removed with a mild anneal.[10]

RELATED EVENTS DURING THIS GRANT

We would like to use this opportunity to detail a number of events that occurred in our lab during the time period covered by this grant. Some of these items were not specifically supported with the funds provided by ONR. Nevertheless, the environment that was made possible with ONR funding was a crucial element that made everything possible, and as such, ONR should take some pride in what has been accomplished.

The first, and perhaps the largest, event was the introduction of the scanning force microscope. Support from ONR allowed us to build the environment that attracted Gerd Binnig from IBM/Zurich. During his stay at Ginzton, Binnig was able to demonstrate the principle of the force microscope. He showed that a sharp tip mounted on a cantilever could be used to measure the force between the tip and the substrate. In turn, the device could be used to study the surface of insulating materials with a resolution that was unprecedented. Immediately following this, T. Albrecht, working in Ginzton Lab, undertook the task of microfabricating a combined cantilever with anisotropic etching of silicon. The cantilevers, as introduced by Albrecht, are found in virtually all of the force microscopes in use today. It was an immense contribution, almost in league with the concept of the force microscope itself. Today, the force microscope is used throughout the world. It is established as a viable form of microscopy in multiple fields of science and technology.

During this period, we have perfected the techniques associated with the micromachining of cantilevers with integrated tips. We are now able to fabricate cantilevers that contain sensors for monitoring the deflection of the tip. This is done by including a piezoresistive element into

the silicon that comprises the cantilever. It is not quite as sensitive as the optical detection systems, but the latest piezoresistive devices are capable of detecting sub-Ångstrom motion. This is adequate for all but the most sensitive imaging areas.

Finally, we wish to point out that the technology developed under this grant, as well as that associated with the force microscope, has been completely transferred to industry. It is now available in commercial instruments. This includes the UHV STM that was used extensively in our study of semiconductor surfaces, as well as the force microscope. It is a satisfying completion for this work.

FUTURE DIRECTIONS

It is now evident that the scanning probes will permit us to go beyond imaging and use these devices for surface modification. They will be used for a new form of direct write lithography with a resolution that exceeds that now available with optical lithography; they will be used to pattern substrates with line widths in the region of 0.1 μm to 10 nm . There are many labs, such as NRL and the Teckman Institute at the University of Illinois, engaged in this program. The progress during the latter half of 1993 and the first half of 1994 has been remarkable.

It is also evident that scanning single tips over the substrate will severely limit the speed with which these processes can be carried out. In our view, this limitation in speed can be overcome with a parallel array of cantilevers and we have proceeded to move in this direction. At this time we have four cantilevers with integrated tips, integrated sensors, and integrated motion actuators operating in parallel. The four parallel cantilevers will be satisfactory for providing us with the proof of concept. We believe it will be an easy matter to fabricate an array of 100 cantilevers spread over a span of 2 cm . That array will allow us to pattern a full die measuring 2 x 2 cm in a few minutes when we learn to write with a scanning speed of 1 cm/sec . When we develop this form of lithography, it will usher in a new ear for the microfabrication of microdevices on silicon.

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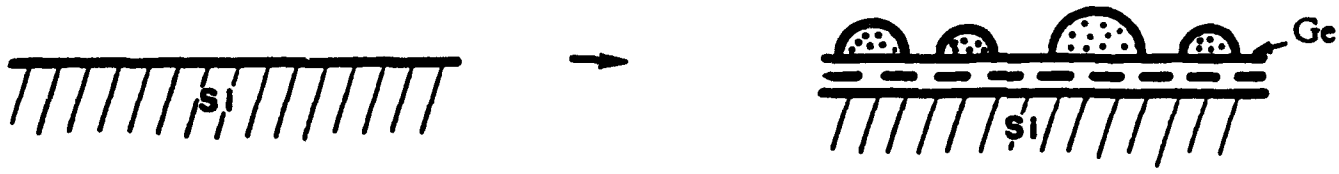
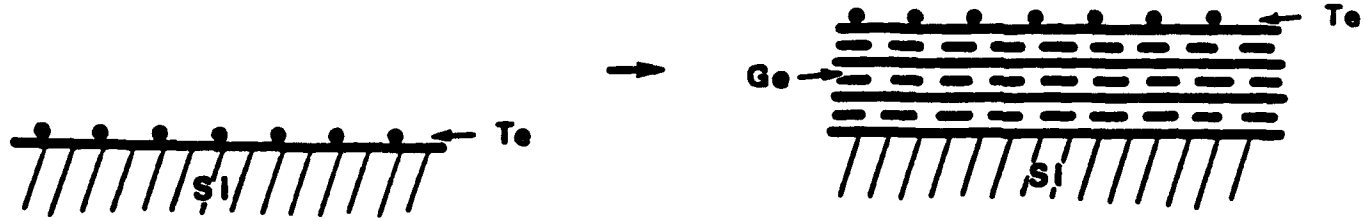


Growth without a surfactant:
Ge/Si grows in the Stranski-Krastanov mode.



Growth with a surfactant:
By depositing Te on silicon prior to the Ge deposition, the Ge can be grown layer-by-layer for several hundred angstroms. The Te segregates to the surface of the growing Ge layer.

Figure 1: Schematic of Ge deposition on Si with and without surfactant.

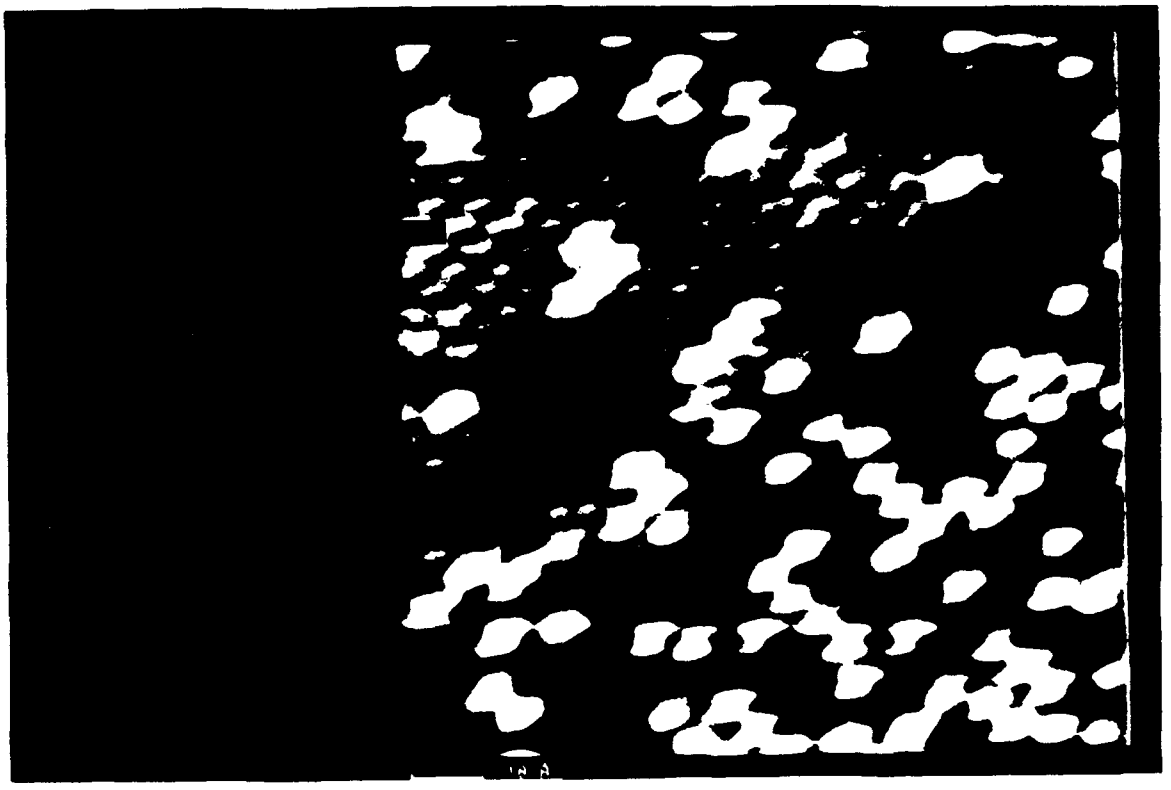


Figure 2: Empty state STM image of 0.1 ML Te/Si(100) deposited at RT.

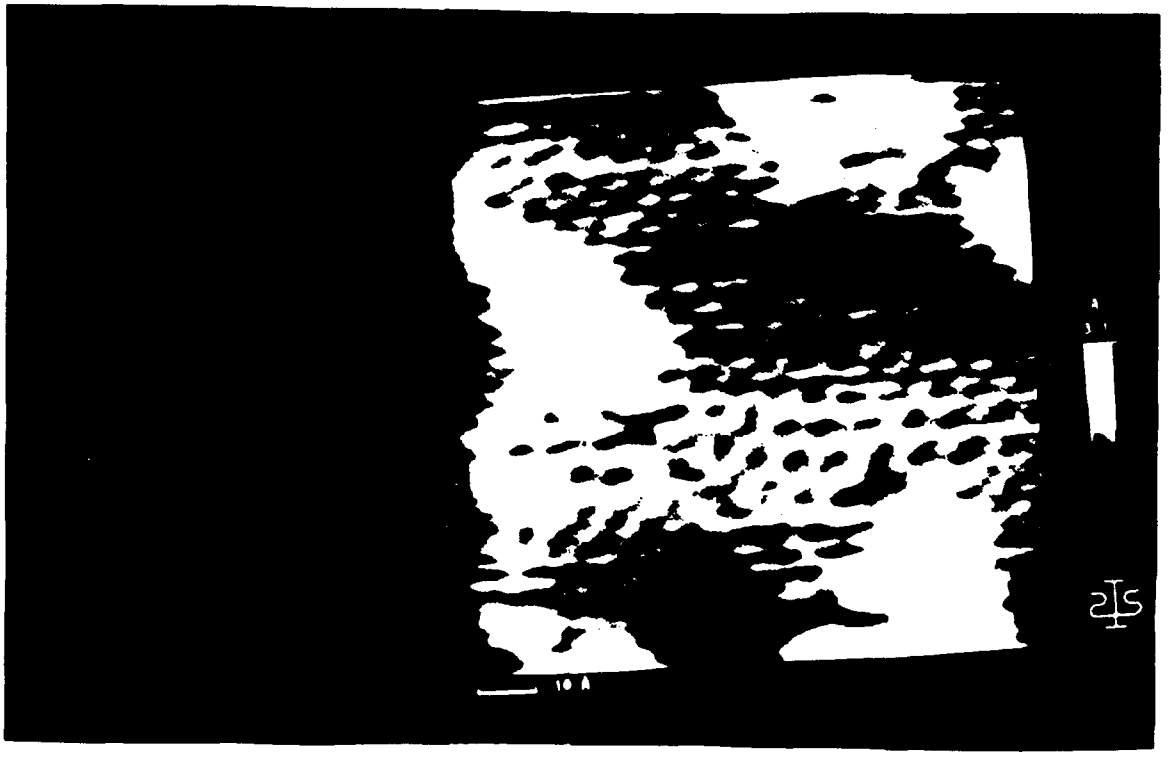


Figure 3: Filled state STM image of 0.1 ML Te/Si(100) deposited at RT and annealed at 400^{o}C for ten minutes.

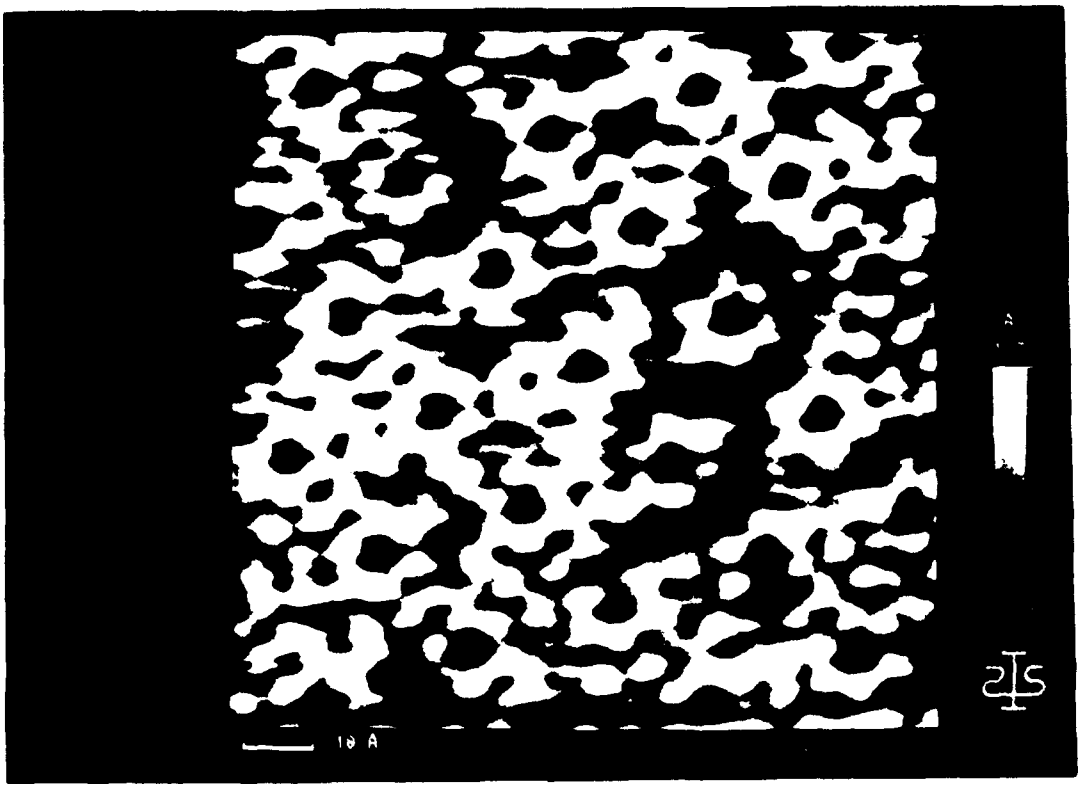


Figure 4: Empty state STM image of 0.15 ML Te/Si(111) deposited at RT.

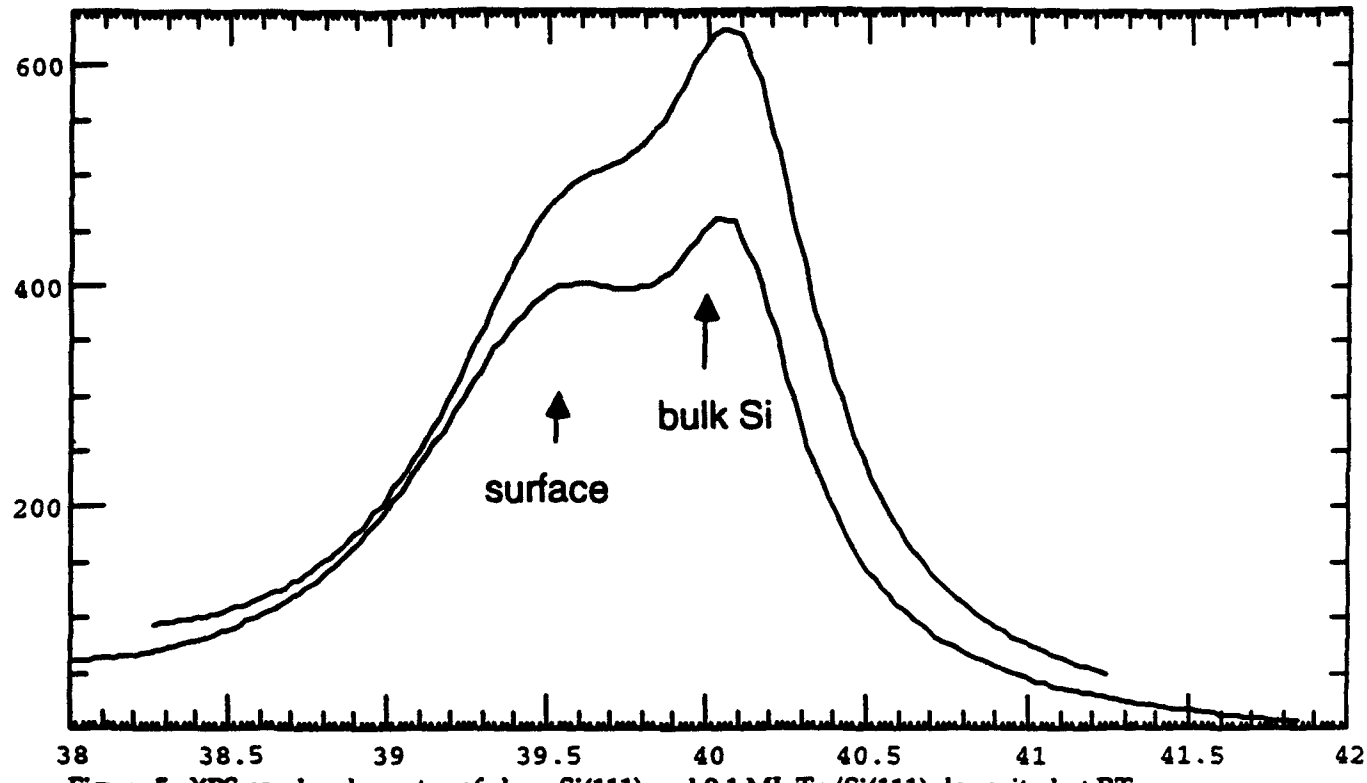


Figure 5: XPS corelevel spectra of clean Si(111) and 0.1 ML Te/Si(111) deposited at RT.

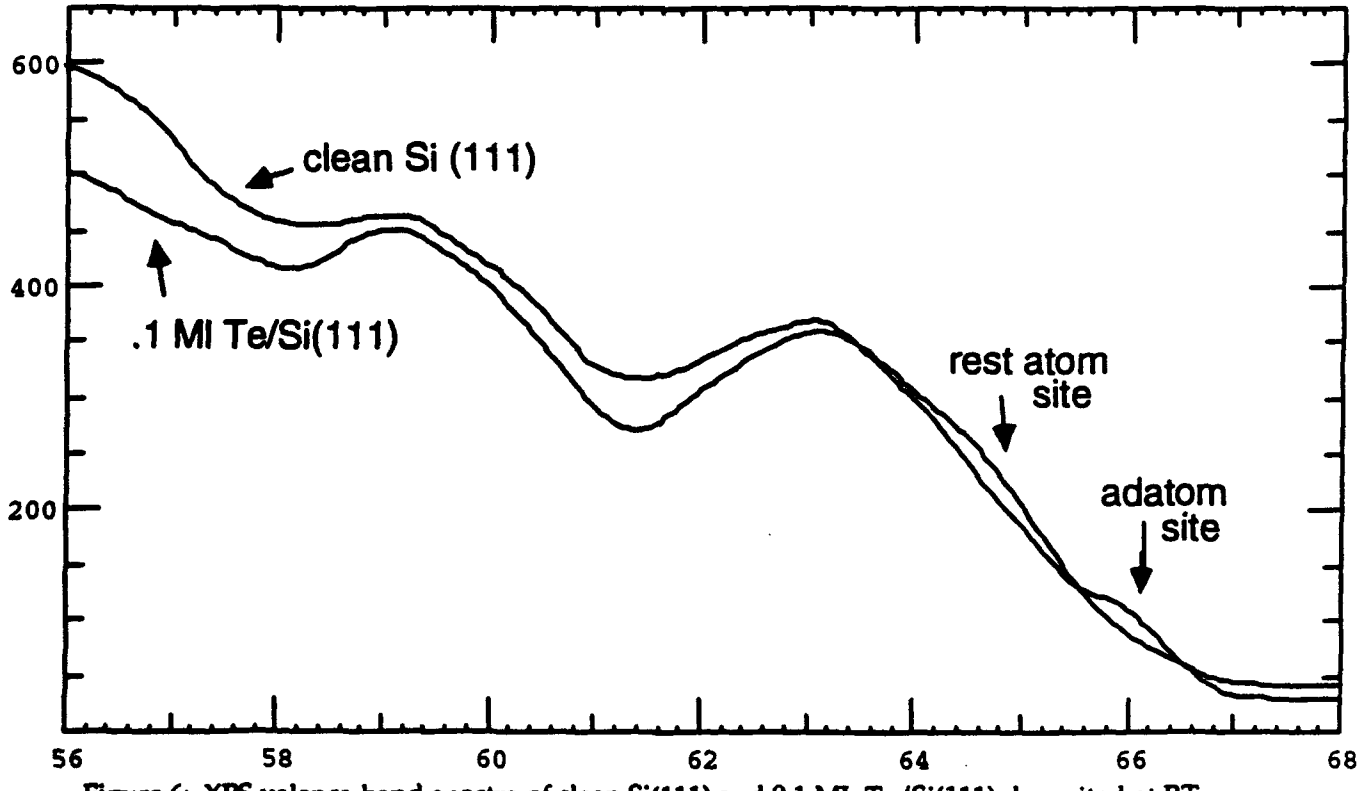


Figure 6: XPS valence-band spectra of clean Si(111) and 0.1 ML Te/Si(111) deposited at RT.